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1949.ACTIVITIES AT JUNE MEETINGS OF DEPARTMENT OF CHEMICAL SCIENCES

S. V. Shevelev

A general meeting of the Department of Chemical Sciences of the Academy of Sciences USSR, devoted to organizational problems, was held 3 June 1949.

Aleksandr Vasil'yevich Topchiyev was elected by secret ballot to active membership in the Academy of Sciences USSR in the Department of Chemical Sciences.

Three institute directors whose terms had expired were re-elected by secret ballot to their posts. They were Academician A. N. Nesmeyanov (Institute of Organic Chemistry), Academician N. N. Semenov (Institute of Chemical Physics), and Academician V. G. Khlopin (Radium Institute). Before the unanimous vote was cast, the Board of the Department of Chemical Sciences had suggested that the terms of these three men be extended.

Since the majority of the board members had come to the end of their terms in office, 11 men were elected by secret ballot to new terms. These were Academicians A. N. Nesmeyanov, S. I. Vol'fkovich, N. N. Semenov, V. G. Khlopin, V. M. Rodionov, I. I. Chernyayev, I. V. Grebenshchikov, A. N. Frumkin, and A. V. Topchiyev, and Corresponding Members A. P. Vinogradov and V. I. Spitsyn. S. I. Vol'fkovich was unanimously designated Deputy Academician-Secretary of the department.

Besides the 11 men who are beginning new terms, Academician M. M. Dubinin, Academician-Secretary of the department, and Corresponding Member I. N. Nazarov, Deputy Academician-Secretary, are serving terms which have 2 years yet to run.

At another general meeting of the department on 6 June, two reports were presented. Corresponding Member N. A. Izgaryshev discussed the relationship of the processes of electro-oxidation to the nature of cations. His investigations dealt with the influence on the progress of electrode processes of neutral ions, i.e., those ions which are present in electrolyzed solutions but which may not be directly related to the basic electrodic process.

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Izgaryshev made a comparative study of anode processes in the electrolysis of chlorides of magnesium, calcium, barium, lithium, sodium, potassium, rubidium, and ammonium. He examined those processes both by methods of chemical analysis and by the method of polarization curves, and established the possibility of conducting continuous electrolysis in cells under constant conditions to the point of formation of perchlorates for all of these chlorides except rubidium and ammonium chlorides.

The most rapid and complete conversion of the chlorides to perchlorates was noticed in the cases of lithium, calcium, and barium chloride. Less rapid and less complete conversions were noted for potassium and sodium chloride. A study of the results of the experiments with the former group of chlorides established that the smaller the radius of a cation, the greater the favorable influence it exerts on a process of formation of perchlorates. Study of the second group showed that the greatest favorable influence was exerted by the calcium cation.

Analogous research was conducted also in the study of the anode process taking place in the preparation of persulfates from potassium, sodium, ammonium, lithium, magnesium, zinc, and aluminum sulfates. The most rapid and complete conversion of sulfates to persulfates was observed for the ammonium and calcium salts. Persulfates were not formed in the cases of zinc and aluminum salts, and in these cases the anode process resulted only in the liberation of oxygen. The rate of formation of persulfates and the amount yielded per ampere hour was increased along with an increase in the radius of the cations, and, consequently, in line with a decrease in their potentials, their effect on the ionization in solution, and their energies of hydration. Fluorine ions have a very favorable effect on the formation of persulfate. At this point the author produced earlier data of his own on the theory of the effect of fluorine ions on anodic overvoltage during the electrolysis of sulfates; he also introduced other data from original previous research. In the ensuing discussion Academicians A. N. Frumkin and S. I. Vol'fkovich, Corresponding Members A. S. Kapustinskiy, A. I. Brodskiy, B. V. Nekrasov, V. I. Spitsyn, and I. A. Kazarnovskiy, and others participated.

The second report, "Photochemical Reactions of Chlorophyll and Phthalocyanins," was presented by Academician A. N. Terenin and Doctor of Chemical Sciences A. A. Krasnovskiy, who acknowledged work done by A. N. Bakh, M. S. Tsvet, and K. A. Timiryazev. They stated that Timiryazev first propounded the theory of the sensitizing action of chlorophyll based on its reversible chemical conversion.

Terenin and Krasnovskiy in experiments used oxygen and dyestuffs with different oxidation-reduction potentials as oxidizers and used ascorbic acid and a number of other compounds as reducing agents. They succeeded in establishing the formation of unstable products from the interaction of the pigment (chlorophyll or magnesium phthalocyanine) with oxygen and organic peroxides. They did not, however, observe any evidence of the dehydrogenation of chlorophyll as a result of interaction with other oxidizing agents. They observed for the first time the formation of products of photochemical reduction of chlorophyll as a result of its interaction with ascorbic acid and other compounds in the absence of atmospheric oxygen in a medium of organic bases. This unstable product of reduction (probably of the semiquinone type) is very active chemically and in darkness enters into a reversible reaction with a number of compounds.

To obtain data on the mechanism of chlorophyll-sensitized oxidation (with oxygen), two types of reactions were investigated: (1) the oxidation of oleic acid proceeding through the step in which oxygen is added under peroxide formation, according to A. N. Bakh, and (2) the oxidation of ascorbic acid to form hydrogen peroxide and dehydroascorbic acid. The authors showed that both compounds are capable of interacting with photochemically formed products of

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oxidation of the pigment, and that the product of photoreduction of the pigment reacts in darkness with oxygen. The dominating mechanism of the process depends on the character of the medium, e.g., in pyridine the predominant reaction is that of photoreduction. In alcohol, the main reaction is oxidation.

Academician S. I. Vol'fkovich, Corresponding Members A. I. Brodskiy, S. N. Danilov, A. A. Grinberg, I. A. Kazanovskiy, and K. V. Chibisov, and others took part in the discussion which followed.

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